

7: Carbon-based Compounds and Exobiology

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7.1. SCIENTIFIC OBJECTIVES

The ultimate issue in this area concerns life: Is there evidence anywhere in the solar system besides Earth for life, either extant or extinct? *COMPLEX* (1994) concluded that "Further study of Mars, with its record of abundant liquid water early in its history, is of major importance in regard to the origin of life. Whether or not evidence is found for extinct, or even extant, organisms, the exobiological exploration of Mars will lead to a more constrained definition of the planetary conditions that constitute a 'window of opportunity' for the emergence of life." Furthermore, *COMPLEX* noted that "Organic materials are thought to be significant components of comets Such substances and the mechanisms that form them likely contributed to the pool of organic chemistry that led, on Earth, to life." These considerations led *COMPLEX* to pose the following questions to be addressed by space missions during the 1995–2010 time frame:

Did Mars ever accumulate a reservoir of prebiotic organic compounds, and does any trace of such material remain on Mars today? Is there any evidence that organic matter underwent prebiotic chemical evolution on Mars?

Did life emerge on Mars and, if so, did it leave any record of extinct life forms? Is there any evidence for life on Mars today?

[What is] the population of carbonaceous materials in cometary nuclei?

7.2. MEASUREMENTS/OBSERVATIONS NEEDED AT MARS

The scientific objectives listed above translate into a series of measurements and/or observations to be performed by landed spacecraft. (Note that these measurements/observations should follow a reconnaissance phase of exploration employing a series of orbital spacecraft.) The following measurements/observations, in no particular order of priority, are considered necessary for the exobiological exploration of Mars:

1. Detailed assessment (mineralogical, chemical, and textural) of rock diversity at a landing site. This is a necessary early step in the search for either extinct or extant life. It is also of importance in the study of prebiotic chemical evolution.

2. Chemical characterization of the materials at a local site. Of interest are the elemental abundances in rocks and in surficial deposits of fine materials, focusing on the rock-forming elements and C.

3. Abundance of H at any accessible sites. In most cases, this will be present in chemically combined form as a hydrated lithology, though it may be possible to find a location where subsurface ice is accessible by drilling beneath a landing site.

4. Identification of specific minerals that would be diagnostic of aqueous processes. Such minerals would include carbonates, cherts, evaporites, and phosphates.

5. Textural examination of lithologies thought to be formed by aqueous activity. Such textures could be characteristic of the mode of secondary alteration and potentially indicative of fossiliferous lithologies.

6. Search for minerals that might have been produced as a result of biological processes, such as phosphates, manganese oxides, and certain carbonates.

7. Mapping the distribution, in three dimensions, of the oxidant(s) identified on the martian surface by the Viking mission.

8. Definition of the local chemical environment. Available chemically reactive species in the upper surface would be assayed, as well as the nature of the environment when moistened or wetted, including pH, Eh (oxidizing potential), ionic strength, presence of micronutrients, and other aspects of the soils and soluble minerals.

9. Determination of stable-isotope ratios for the biogenic elements (C, H, O, N, and S) in surficial mineral deposits, e.g., evaporites. This would provide an additional constraint on volatile history and reservoirs.

10. Quantitative analysis of organic (= noncarbonate) C.

11. Elemental and isotopic composition (C, H, O, N, and S) of bulk organic material.

12. Search for specific organic compounds that would yield information about synthetic mechanisms, in the case of prebiotic evolution, and about possible biomarkers, in the case of extinct or extant life. Key compound classes for which evidence should be sought include lipids, amino acids, and carbohydrates.

13. Coring, sampling, and detection of entrained gases (CH_4 , H_2 , H_2S , etc.) and cosmic-ray-induced reaction products (e.g., HCOH) at the polar ice cap.

An Exobiological Strategy for Mars Exploration (NASA SP-530) concluded that "The most immediate [surface] instrumentation needs are the following: design and construction of instrumentation for *in situ* mineralogical identification, description of the microenvironment (including oxidant distribution), and detection and characterization of organic matter; development of a capability for acquiring samples from a depth of several meters in the regolith and from the

interiors of rocks; and early deployment of the above." Later stages of the exobiological exploration of Mars would likely involve more highly focused biological experiments, such as a search for morphological fossils and/or tests for active metabolism, such as were flown on the Viking landers. Positive results from such experiments would undoubtedly lead to biologically focused sample return missions.

7.3. MEASUREMENTS/OBSERVATIONS NEEDED AT A COMET NUCLEUS

Unlike the case for Mars, there is little doubt that organic compounds are ubiquitous within cometary nuclei, and that they are of interest in their own right, rather than as a result of their possible involvement in biological processes. There is a large dataset in existence on the molecular composition of cometary comae (Newburn *et al.*, 1991). Groundbased spectroscopic observations have detected numerous molecular species, and these data have been augmented by both spectroscopy and mass spectrometry from the Giotto and Vega missions to Comet Halley. Water makes up about 80% of the volatile content of Comet Halley, and possibly up to 50% of the mass of the nucleus. Other molecules of prebiotic interest detected in cometary comae include CN and HCN, CO, CO₂, CH₃OH, HCOH, and NH₃. Many of the molecules observed in cometary comae are probably ionized fragments of larger parent molecules that are condensed on the surface of the nucleus. The identities of these parent molecules are not known, since the presence of the coma makes it virtually impossible to observe the comet surface directly, even from nearby spacecraft.

The dust in the coma of Halley has been examined by mass spectrometers on board both Giotto and Vega. Of primary interest to exobiology is the detection of "CHON" particles, dust particles containing C, H, O, and N. Intermediate-mass organic macromolecules have also been detected in the coma, with mass spectra indicating repeating 14–16 amu units in a linear polymeric structure. These data have been interpreted as a signature of either hydrocarbons, with a $-(CH_2)_n$ - structure, or polyoxymethylene (POM), a polymer of formaldehyde, with a $-(CH_2O)_n$ - structure. The $^{13}C/^{12}C$ ratio of C₂ and CN in the coma of Halley is approximately solar (with a rather large uncertainty), but a significant proportion of CHON grains analyzed by the Giotto and Vega spacecraft revealed substantial enrichment in ^{12}C , suggesting an interstellar source for some cometary organics.

The following measurements/observations are considered necessary during the exploration of a cometary nucleus:

1. Abundances and stable-isotopic compositions of biogenic elements (C, H, O, N, and S). In addition to bulk measurements, evidence of spatial inhomogeneity should be sought.

2. Identification and quantitative determination of individual species within major classes of organic compounds.

Such information will aid in discriminating between possible synthetic and/or alteration mechanisms.

3. Isotopic analysis (for C, H, O, N, and S) of specific organic compounds. This information will assist in identification of source regions for different organic compounds.

4. Isotopic analysis of all volatile phases. Such information would help clarify the source region(s) of the major components of the cometary nucleus and could reveal evidence of subsequent processing of cometary volatiles, possibly including organics.

7.4. MEASUREMENTS/OBSERVATIONS ON OTHER SOLAR SYSTEM OBJECTS

Although Mars and cometary nuclei constitute the most promising surface sites within the solar system to pursue exobiological questions, the C-based chemistry of several other objects should not be overlooked. (The organic chemistry of Titan has attracted much interest, but it seems likely that the Cassini mission will address many of the outstanding issues in that area, and, furthermore, the feasibility of conducting surface science *sensu strictu* on Titan is problematic at this time.)

7.4.1. Moon

Analysis of Apollo samples showed that lunar rocks are essentially devoid of C but that the regolith contains significant quantities (up to about 100 µg C/g) that are believed to be largely, and possibly wholly, of solar wind origin. This regolith C reveals a wide range in $\delta^{13}C$ value, from a few per mil below the terrestrial standard to about 20‰ above. These values fail to correlate with any other known parameters, so this issue certainly deserves further study. It seems likely that sample return will be needed for such studies, but the possibility of developing sufficiently sophisticated robotic experiments should not be ignored.

The very low O fugacity characteristic of lunar rocks suggests that indigenous water has not existed within the Moon during its history. Prospects for aqueous chemical evolution on the Moon therefore seem to be ruled out.

7.4.2. Asteroids

The majority of astronomically observed asteroids reveal spectral evidence for abundant surface C. In fact, for sampling purposes, it may be that there is an effective continuum from rocky asteroids containing some C to cometary nuclei extremely rich in carbonaceous material. Throughout such a range, the scientific objectives and desired measurements and observations remain essentially the same. We have almost certainly already performed many organic analyses on samples of some of the moderately C-rich asteroids, in the form of carbonaceous chondrites and, possibly, interplanetary dust particles. Whether a landed spacecraft mission to an asteroid could yield exobiologically relevant data beyond

what could be derived from a comet nucleus or from analysis of carbonaceous chondrites is problematical.

7.4.3. Europa

It has been remarked on several occasions that fissures on the surface of Europa may be the only place in the solar system outside the Earth where liquid water might be in contact with both carbonaceous material and sunlight. It follows that such places could be sites of organic synthesis that, while not likely to lead to emergence of life, could nonetheless be of interest to exobiology.

7.5. AVAILABLE INSTRUMENTATION

Table 7.1 lists the instrumentation currently available for addressing exobiological objectives on planetary surfaces. Note that not all the techniques listed generate key exobiological data; several are needed for obtaining important environmental information and/or site or sample characterization during earlier stages of exobiological exploration. We shall discuss, in alphabetical order, the techniques listed in Table 7.1, focusing mainly on key exobiological experiments within the context of Mars exploration, but including where relevant their employment in other planetary settings.

7.5.1. Alpha-Proton-X-Ray

Perhaps more than any other material, the fine martian dust embodies the end products of impacts, weathering, volcanism, and aqueous activity. How extensive were the contributions of aqueous weathering, and therefore how pervasive on Mars were those aqueous environments that might have hosted the origin of life on Mars? With its broad coverage of the elements, α -proton-X-ray (APX) should give us a better estimate of the chemical composition of martian fines relative

to the composition of basalts or the highland materials. If liquid water were a key erosional agent, then chemical separations of the elements should occur when igneous rocks disaggregate to form shales and chemical precipitates, as on Earth. For example, aluminum is strongly fractionated relative to calcium and other alkaline-earth elements by aqueous alteration of igneous silicates. APX analysis is discussed in detail in Chapter 2.

7.5.2. Aqueous Chemistry on Mars

Because a principal focus of exobiology is to understand the extent to which liquid water has modified the martian crust, it seems relevant to assess the composition of a water solution that has been in contact with the martian soil (Clark, 1994). In addition to learning more about soil composition, such an experiment might help to establish the extent to which this composition can be attributed at least in part to a history of chemical weathering. Perhaps evidence for pervasive chemical weathering indicates that indeed Mars' early environment was well suited for chemical evolution.

Upon addition of water, determinations should be made for the pH, Eh, enthalpy of solution, and evidence for soluble minerals (especially salts) and trace elements. Soil properties such as absorptivity and particle-size distribution should also be determined. Such measurements could be achieved in a flight instrument because an array of chemical microsenors are now available. In addition to Eh sensors, ion-specific electrodes can be deployed to measure pH, soluble anions (e.g., chloride, sulfate, carbonate), and cations (Ca, Fe, Mg, K, Na, etc.). It would be useful to treat the soil with pure water and with an acidified solution in order to extract less-soluble minerals (e.g., certain carbonates and sulfates) that still might have been deposited in aqueous environments.

The presence and nature of clays in the martian soil are also quite relevant for assaying the history of water activity on the planet. Methods for measuring particle-size distribution and adsorption characteristics of soil particles would be informative. Such an instrument would have to address several technical challenges associated with maintaining liquid water in the martian surface environment, with its low pressures and temperatures. Additional challenges are associated with the selection of the most robust microsenors and methods for measuring soil grain size.

7.5.3. Gamma-Ray Spectroscopy

The technique of γ -ray spectroscopy relies on the detection and quantitation of natural γ radiation emitted by planetary material. The elements whose abundance can thereby be measured are either those with long-lived radionuclides (e.g., K, Th, U) or those that generate γ rays when exposed to cosmic-ray-produced neutrons (e.g., O, Na, Mg, Si, Cl, Ca, Mn, Fe, and Ni). When used in conjunction with neutron spectroscopy, as is commonly done, this technique also yields the abundance of H, i.e., in most cosmic settings, the abun-

TABLE 7.1. Instrumentation currently available for addressing exobiological objectives on planetary surfaces.

To obtain:	An Understanding of Planetary Environment	Identification of Key Sample	Key Chemical or Morphological Measurement
Alpha-proton-X-ray	X	X	
"Aqueous chemistry"	X		
Gamma-ray spectroscopy	X		
Gas chromatography	X	X	X
Imaging	X	X	X
Infrared spectroscopy	X	X	X
Mass spectrometry (isotopes)	X	X	X
Mass spectrometry (organics)	X	X	X
Mössbauer	X	X	X
Neutron activity	X		
Neutron spectroscopy	X		
Raman spectroscopy	X	X	
Scanning electron microscopy		X	X
Secondary ion mass spectrometry		X	X
Thermal analysis	X	X	X
X-ray diffraction/fluorescence	X	X	X

dance of water. It is this feature that makes it of such importance to exobiological exploration. Gamma-ray spectroscopy is described in more detail in Chapter 2.

7.5.4. Gas Chromatography

Gas chromatography (GC) is a powerful and reliable technique for the analysis of gaseous mixtures. Because of its reliability it has been one of the most useful analytical methods used in planetary exploration missions to Venus by the Pioneer Venus spacecraft and Mars by Viking (*Oyama et al.*, 1980; *Oyama and Berdahl*, 1977). Moreover, the utility of GC has been proven for determining gaseous components evolved during pyrolysis, both terrestrially and during landed missions to Mars (Viking). Volatiles of primary interest to exobiology are those that contain the biogenic elements and include organics, water, CO_2 , NO_x , NH_3 , H_2S , and SO_x .

In the vast majority of gas-chromatographic determinations, a sample is introduced at the head of a chromatographic column. This column is usually packed or coated with a stationary phase. As the sample is carried through the column by a gas stream (the carrier gas), it is physically separated into discrete bands by the process of differential migration, based on the differences in the abilities of the gases within the sample to adhere to the stationary phase of the column as it passes through it. At the end of the column the separated bands emerge, each containing a component of the mixture, and are measured by a general-purpose detector. Identification is determined by the retention time of a compound on a given column, which is commonly unique, though it can vary with some analytical conditions (*Pollock et al.*, 1982; 1984).

General broad-range detectors include the common thermal-conductivity detectors (TCD) and the metastable ionization detectors (MID). TCDs have been used as detectors in GCs that have conducted analyses during the Viking and Pioneer Venus missions. In a TCD, as a sample of gas passes into the detector it changes the thermal conductance within the detector. The change in conductance is transformed into a voltage, the size of the voltage being proportional to the quantity of the gas flowing through the detector. In the MID, the carrier gas (usually one of the noble gases such as He, Ne, or Ar) is ionized. As a gas sample passes through the detector, the ionization potential of the detector changes. The change in ionization potential is transformed into a voltage that is proportional to the quantity of gas flowing through the detector (*Woeller et al.*, 1984). The advantage of the MID over the TCD is that it is usually 2–3 orders of magnitude more sensitive to most gases.

Coupling DTA (see section 7.5.16) with GC enables one to detect the physical changes associated with the volatilization of certain substances, providing substantial additional information that synergistically couples with the DTA data. Specifically, the data from the GC will unequivocally identify any evolved gases such as CO_2 , H_2O , organics, etc., and will allow one to correlate DTA events with the specific gases evolved during that event. The combination of thermal and

evolved gas analysis distinguishes between phase changes and chemical reactions that evolve water, CO_2 , or other volatiles (e.g., complex mixed organics). By relating the gases evolved from minerals, as identified by GC, and the DTA temperature at which gas evolution occurred, it is possible to distinguish among closely related soil components such as clays, zeolites, and silicates as well as evaporites (*Banin et al.*, 1993).

An example of the necessity of determining if a gas is evolved during a thermal reaction of soil is that shown when quartz is heated. Quartz is identifiable by its sharp endothermic α to β transition occurring at 580°C . This transition occurs within the same temperature range as the broad endothermic water-producing dehydroxylation reaction of clays. Because the dehydroxylation reaction in clays is broad and produces water vapor that can be detected by a gas chromatograph, whereas the quartz transition reaction is sharp and produces no gas, they are easily distinguished in the sample using DTA/GC, but difficult to distinguish in the same sample using either DTA or DSC alone. The advantage of a GC over specific compound detectors (such as those for CO_2 , H_2O , etc.) is that if an unanticipated gas is produced, an instrument equipped with specific compound detectors will not be able to identify it, but a GC, with its broad analytical range, can, provided the appropriate standards have been run. The evolution of several gases simultaneously from a single reaction (an unlikely event) is easily dealt with by the inherent capability of the GC.

7.5.5. Imaging

Clearly a lander camera would be crucial for locating rocks whose formation involved liquid water. On Earth, such chemically precipitated sediments constitute no more than a few percent of the very ancient (early Archean age) rock sequences that have been examined. Thus, boulder fields must be surveyed extensively for the “right” rocks. Once prospective rocks have been located, a closer inspection of their textures would reveal more details about their environments of deposition. For example, sedimentary layers, grain-size distributions, and even preliminary identification of minerals would all be facilitated by a hand-lens type of imager. In principle, fossils might be located using a remotely deployed microscope; however, this strategy probably offers only a low chance of success. On Earth, fossiliferous rocks usually require extensive preparation (thin-sectioning, etc.). Furthermore, locating microfossils usually requires considerable searching of ancient rocks. The detection and confirmation of a fossil occurrence will probably require a sample return or human mission to Mars. Cameras, including the hand-lens type, are discussed in Chapter 9.

7.5.6. Infrared Spectroscopy

Perhaps the most promising site for extant life on Mars today is in a subsurface aquifer where water has been maintained in its liquid state by geothermal heat. A definitive

demonstration that volcanism or hydrothermal activity persists today would help to strengthen the evidence for this possibility. Perhaps atmospheric trace gases would be the most accessible line of evidence for such subsurface activity. Gases such as CH_4 , SO_2 , etc. are prospective candidates that might be detectable by infrared observations of the atmosphere. Regarding the search for evidence of extinct life or prebiotic chemical evolution, imaging of surface materials in the near- and midinfrared could help to survey rocks in the vicinity of the lander or rover to facilitate sampling of carbonates and other lithologies of exobiological interest.

Infrared spectroscopy has also proven to be a useful tool in remote sensing of planetary atmospheres and surfaces. In particular, remote sensing of several planetary bodies using near-IR spectroscopy (NIR) has provided information on the chemical constituents on their surfaces, e.g., condensed SO_2 on the jovian moon Io, CH_4 , CO_2/CO , N_2 ices on Triton and Pluto, and O_2 on Ganymede. Similar studies are likely to be of value in analyzing the constituents of a cometary nucleus.

The near-IR (0.8–5 μm) region displays characteristic features associated with the combination and overtones of bond stretches, bends, etc., as well as the fundamental C-H stretches of hydrocarbons. There is considerable difference in the frequencies of the bands associated with aromatic and aliphatic groups. A typical spectral resolution of 2–5 cm^{-1} is adequate to distinguish between different components. In the 2–2.5- μm region, the spectra provide information on H_2O ; water of hydration and H_2O bonded internally to inorganic salts can be easily distinguished. Most inorganic ions, like CO_3^{2-} , NO_3^- , and PO_4^{3-} , have strong fundamental modes in the thermal-IR region and their overtones fall in the near-IR range. Use of fiber optics can permit probing beneath a weathered veneer.

Thermal-IR spectra also provide a sensitive technique for the identification of surface constituents. Such an instrument may be employed in emission mode, if there is an inherent temperature gradient near the surface, or in reflectance mode using solar radiation as a source. An instrument operating in the range 2–25 μm , with a signal-to-noise ratio of 400, is being developed for use on the martian surface (Christensen *et al.*, 1992).

A prototype miniaturized NIR laboratory-scale instrument has been developed commercially (SpectralChem 100, AnalytiChem Corp.). This weighs less than 5 kg but has a power requirement of 60 W. For use on a lander/rover, this power consumption needs to be reduced. One of the advantages of NIR spectroscopy is that in weakly absorbing regions the radiation penetrates deeper into the surface, enabling components below the surface to be investigated.

7.5.7. Mass Spectrometry (Isotopes)

Stable-isotopic measurements of the “biogenic” elements, C, H, O, N, and S, can in many instances be utilized to gain insights into those processes that have affected the reservoirs

of these elements in a planetary environment. For example, the atmospheric H budget on Mars can be examined using stable-isotopic abundances (e.g., Donahue, 1995). Isotopic measurements are significant to exobiology for several reasons. First, such measurements might help us to reconstruct the atmospheric composition, hence the environmental conditions, during the first 0.5–1.0 G.y. of martian history (e.g., Owen, 1992). It was during this putatively more-clement period that liquid water apparently persisted on the surface and the opportunity was best for martian life to begin. Second, isotopic analyses of surface materials might help to characterize any materials that contain biogenic elements and to determine whether these samples formed in equilibrium with the current atmosphere. For example, a carbonate rock with $^{13}\text{C}/^{12}\text{C}$ value significantly lower than that expected at equilibrium with the atmosphere might have formed during an earlier epoch, when the atmospheric isotopic composition had been perhaps less fractionated by processes involving loss of C to space. This earlier epoch might have had a climate more suitable for chemical evolution or life, therefore the carbonate might also contain material of significance for exobiology. Third, if any organic matter is detected, either on Mars or on the surface of a comet, stable-isotopic measurements might help to infer the processes responsible for its origin. For, example, this approach might identify components on a comet that originated from outside our solar system by detecting anomalous $^{13}\text{C}/^{12}\text{C}$ values. In another example from early Earth, $^{13}\text{C}/^{12}\text{C}$ values of organic C are lower by typically some 2–4% than the corresponding values in carbonates. This particular depletion is characteristic of biological organic synthesis. Such a measurement might detect whether a characteristic pattern exists on Mars that could implicate a particular mechanism (biologic?) for organic synthesis.

Stable-isotopic measurements are best performed using magnetic-sector or quadrupole mass spectrometers. Miniaturized mass spectrometers have been built routinely for spaceflight applications (e.g., Niemann *et al.*, 1992). Atmospheric measurements of CO_2 on Mars could be performed using a stand-alone mass spectrometer. An instrument with mass resolution ($M/\delta M$) of at least 200 and a precision for the isotopic measurement of perhaps 1% is necessary to provide meaningful constraints for models estimating either rates of loss to space or to estimate exchange rates with crustal reservoirs. Of particular interest are recent developments that promise to effect significant weight reductions in isotope mass spectrometry by means of two different approaches: the construction of a “mass-spectrometer on a chip” (Young *et al.*, 1994) and the use of tunable diode-laser spectroscopy (Sauke and Becker, 1994).

Measurements of C, H, O, N, and S species in crustal materials would require that a device liberate gases from these materials and deliver them to the mass spectrometer. Heating the sample of martian rock or soil, or cometary

regolith might be one such approach. Isotopic measurements of organic C should have an associated precision of 1% or better in order to interpret mechanisms of organic synthesis or to detect exotic sources of C (such as those originating from outside the solar system). For organic analyses, the sample also must be combusted (or the sample heated and the evolved gases combusted) to obtain the isotopic measurement. In some cases, where the soil is heated, gases that coevolve might also have overlapping mass spectra, which could interfere with the isotopic analyses. Some provision must therefore be made to reduce this interference. Chemical trapping or gas chromatography to separate the gases would be effective. For example, an appropriate system for analyzing the stable-isotopic composition of a sample might include analytical components that (1) liberate the elements as gases (e.g., a heater), (2) separate the gases (gas chromatograph), (3) combust any reduced or oxidized species to CO_2 and N_2 (oven with catalyst), and (d) perform the isotopic measurement (mass spectrometer).

7.5.8. Mass Spectrometry (Organics)

Mass spectrometry (MS) is a powerful instrumental technique for organic analysis on a planetary surface because it is the only major organic analytical technique that can detect, identify, and quantify most classes of organic compounds. Small, neutral, volatile organics such as HCN and HCOH could be detected in solar system ices by direct MS. In a low-temperature, volatile-rich environment such as a comet nucleus or martian polar cap, a sample of ice potentially containing organic molecules could be simply warmed under vacuum until volatilized and injected directly into the mass-spectrometer ionization source. The use of soft-ionization techniques, which generate molecular ions without fragmenting the molecule, would allow a first-order inventory of volatile organic compounds to be quickly carried out. Soft ionization, however, might add significantly to the weight, cost, and complexity of the instrument. A hard-ionization technique such as electron ionization, which fragments the analyte molecule but requires less complex instrumentation, could be coupled with groundbased computer-aided mass-spectral analysis to identify volatile organics. Amino acids, purines, pyrimidines, and other nonvolatile prebiotic compounds could not be detected by this method. For more-highly-altered samples, such as martian regolith or cometary-nucleus lag deposits, mass spectrometry can be coupled with thermal-analysis techniques to achieve either simple quantitation of total organic C or, with limited thermal exposure, identification of some structural elements of the original analyte.

Identification of nonvolatile organic species can best be achieved when MS is coupled downstream from a molecular separation system, allowing a mass spectrum of each species in the sample to be obtained independently. The only molecular separation technique flown on a spacecraft so far is gas chromatography. In most cases a quadrupole mass spectrom-

eter is used as a chromatographic detector, although other MS types can also be used. The utility of gas chromatography coupled with mass spectrometry (GC/MS) for planetary-surface organic analysis was convincingly demonstrated by Viking (*Biemann*, 1979). The GC/MS on board each of the two landers was the only instrument capable of general organic molecule detection and identification, with detection limits in the parts-per-billion range. This capability served as an important control for the biology experiments, without which the initial positive results might have been misinterpreted. Chromatographic techniques are also capable of separating optical isomers of chiral compounds such as amino acids. This capability can help answer questions about the origins of biomolecular chirality, and serve as a monitor of forward biological contamination of solar system environments.

The use of any chromatographic separation system, however, introduces additional problems and limitations. One of the drawbacks of GC/MS for spacecraft use is that many prebiotically important compounds, such as amino acids, purines, and pyrimidines, must be chemically derivatized to make them volatile enough for GC separation. A chamber and fluid-handling system for the derivatization chemistry must therefore be provided, adding to the size and complexity of the instrument package. Also, since most derivatization reagents are functional-group specific, one class of organic compounds must be targeted for analysis while others are excluded.

Liquid chromatography (LC) is a molecular separation technique that does not require volatile analytes, since the separation is carried out in the liquid phase. LC usually also requires sample derivatization, however, for the chromatographic separation to be achieved. The volumes of solvents required for LC/MS, and the amount of waste generated, are problematic for spacecraft use. Capillary electrophoresis (CE) separates molecules by electrophoretic mobility in a liquid buffer system, and can be performed without derivatization, but the analyte must contain an ionizable functional group. CE/MS can employ chiral mobility modifiers in the separation phase that allow optical-isomer resolution without derivatization, while chiral resolution in GC/MS and LC/MS requires derivatization. Both CE/MS and LC/MS must make use of liquid (generally aqueous) solvents and reagents, so the instrument must be maintained within the spacecraft at temperatures $>0^\circ\text{C}$ and pressures around 1 bar.

The choice of the class of organic compounds to be targeted for analysis is not an easy one. Among the most prebiotically interesting molecules are those that make up modern terrestrial biopolymers. These include amino acids, purines, pyrimidines, sugars, and fatty acids. All these except sugars have been detected in carbonaceous chondrites, and therefore may be present in cometary nuclei and perhaps in some martian environments. It may not be clear, however, whether a given molecule detected on a planetary surface was

formed *in situ* by endogenous organic chemistry or was delivered to the surface by meteorite impact. Organic molecular analysis should be coupled with C, H, O, and N isotope analysis to determine the sources and formation mechanisms of planetary organic compounds.

Mass spectrometers of shoebox size are available and have flown on Viking and Galileo. Recent work in microfabrication of MS systems on single chips holds the promise of even smaller, lighter systems (Young *et al.*, 1994). A single mass spectrometer could be used both as a stand-alone mass analyzer and as a detector for one or more instruments using thermal analysis or molecular separation techniques. LC/MS instruments are now available commercially for laboratory use, and CE systems, including derivatization, if necessary, and injection mechanisms have been fabricated on single glass chips by photolithographic techniques (Jacobson *et al.*, 1994). Continuing advances in miniaturization of these techniques should allow serious consideration of their inclusion in future planetary-surface missions. Target sensitivities for future generations of mass spectrometers should be in the parts-per-billion range, comparable to that of the Viking GC/MS. High mass resolution may be more crucial than high sensitivity for organic-compound identification, and should be no lower than 1 amu, to minimize ambiguities in compound identification.

7.5.9. Mössbauer Spectroscopy

Because a Mössbauer spectrometer will probably be included on lander spacecraft, it is of interest to explore its suitability in an exobiology context. Along with scientific dividends regarding mineralogy and geochemical processes, Mössbauer spectroscopy may also provide clues in the search for fossil evidence of ancient life billions of years ago on Mars.

The Mössbauer spectrum, arising from a nuclear resonance process, depends on the nature of the sample investigated, providing mineral identification and data on oxidation state, particle size, magnetic order, etc. Current planning is to use Fe (^{57}Fe) Mössbauer spectroscopy because of the high natural abundance of Fe. The 270-day half-life of the source, with the ability to start from Earth at high strength, is compatible with a typical mission to Mars, an asteroid, or many comets.

A backscatter Mössbauer spectrometer for lander spacecraft including rovers, under development since 1988, is now sufficiently mature that it is sensible to speak of its near-term deployment. Size and shape are roughly those of a soft-drink can, with mass under 0.5 kg and power consumption less than 2 W. When placed about 1 mm from a surface deposit, for example, by a robotic arm, the instrument can obtain a usable spectrum in 1 to 5 hr.

In exobiological exploration on Mars or asteroids it is of interest to determine the amount of liquid-water alteration of Fe-rich deposits, affecting, for example, the presence of goeth-

ite ($\alpha\text{-FeOOH}$) or hematite ($\alpha\text{-Fe}_2\text{O}_3$), distinguishable by Mössbauer spectroscopy. The technique has demonstrated aqueous alteration in the Orgueil carbonaceous chondrite through the characteristic variation with temperature of the Mössbauer spectrum of the superparamagnetic aqueous-alteration product (Wdowiak and Agresti, 1984).

Perhaps the most exciting potential for Mössbauer spectroscopy is to use it to prospect for minerals in which a bacterial fossil record may reside. At the bottom of Earth's oceans, geothermal vents ("smokers") harbor bacterial communities that derive energy from hot, S-rich vent effluents, something that could have existed on Mars, providing liquid water was then present. Bacteria in outlying regions of such vents are coated with Fe-rich "rust," easily analyzed with a Mössbauer spectrometer. Because bacteria are about a micrometer in size, the Fe-oxide rust must consist of particles about 100 $\times$ smaller (~ 10 nm), "nanophase" particles. When thermal activity ceases, bacteria die, and the rust crystallizes to form a "fossil" with the Mössbauer signature of superparamagnetism, which is a property of nanophase, magnetically ordered material (Agresti *et al.*, 1994).

Sediments associated with Fe-rich hydrothermal springs on land (Yellowstone National Park), which are plausible analogs of what may have existed on Mars and where systematic sample collection is feasible, have demonstrated similar Mössbauer signatures, including deposits of nanophase Fe oxide. The biological influence on deposits collected at YNP, including the ferric/ferrous ratio, reflecting a variation of environmental redox potential possibly due to microbiological diversity with depth (becoming more aphotic and anoxygenic) and/or distance from the vent source (decreasing temperature), is being assessed (Agresti *et al.*, 1995).

All this suggests that, if bacterial-like organisms existed on Mars in a hydrothermal environment, it is likely that these organisms could have also become coated with an Fe-oxide "rust." Conceivably the bacteria may somehow modify the Fe that precipitates on its surface, creating the fine particle structure. Furthermore, photosynthesizing bacteria produce O_2 as a by-product of their metabolism and may drive the precipitation of Fe in these systems. Yet it is still unclear whether nanophase Fe is a sure sign of life or simply an indicator of the type of Fe minerals produced in environments such as thermal springs. The nanophase signature may reflect the rapid rates of crystallization that occur within certain environments. But with Mössbauer it may be possible to distinguish hydrothermal Fe minerals, which would be an important step in exploration for life on Mars. Pinpointing hydrothermal Fe deposits on Mars would assist in the selection of sites for future missions to explore for ancient martian microbes. This strongly argues for using a Mössbauer spectrometer on a Mars lander/rover to look for such deposits. In the laboratory, sample temperature is adjusted by a refrigerator; on Mars, the diurnal (day-night) temperature variation ($\sim 240\text{--}180$ K) accommodates this requirement very nicely.

7.5.10. Neutron Activation

In addition to being a well-known analytical technique in the laboratory, neutron activation can be employed remotely on a planetary surface. The output from a pulsed-neutron generator produces γ rays by inelastic scattering, capture, and delayed induced radioactivity in the material within about a meter of the generator/detector assemblage. Most of the rock-forming elements can be analyzed by this means, plus two elements of particular interest to exobiology: C and H. Pulsed-neutron activation analysis is described in greater detail in Chapter 2.

7.5.11. Neutron Spectroscopy

A further gauge of the importance of aqueous weathering might be revealed by measurements of the H content (as either water or hydroxyl group) in martian fines. At mid to low equatorial latitudes, where no near-surface ground ice is anticipated, much of the H sensed would be bound in salts and clays. Water was detected in the dust by the Viking lander but unfortunately with poor accuracy. A neutron spectrometer should measure this H with much higher accuracy, and thus indicate the degree to which the source rock material has sustained hydration. Neutron spectroscopy is discussed in greater detail in Chapter 2.

7.5.12. Raman Spectroscopy

Laser Raman spectroscopy is used for the analysis of organic (hydrocarbon) as well as inorganic (mineral) substances, making it desirable as an exobiology instrument on a lander spacecraft. Integration of current technologies into a laser Raman system can meet science-yield and spacecraft-compatibility requirements including those for rovers. In the latter context, we envision the use of fiber optics to sense samples at distances as great as 1 km from the spacecraft in which the core of the instrument resides. In addition, Raman can detect, via surface enhancement techniques, species at low concentrations in samples processed (e.g., by gas chromatography) in a small onboard automated "laboratory."

Raman spectroscopy is an optical light-scattering technique for determining the molecular composition of materials or their crystal lattice structure. When light interacts with a material, almost all the light is scattered elastically (Rayleigh scattering) with no change in energy (or frequency). A tiny fraction, 10^{-8} to 10^{-12} , of the incident radiation is scattered inelastically, with loss (or gain) of energy to molecular and lattice vibrational modes. A laser illuminates the sample, the resulting wavelength shift of the scattered radiation being detected using two components: a dispersive element and a photon detector. The spectral shifts are related to molecular structure in essentially the same way as the absorption transitions observed in infrared absorption spectroscopy. Selection rules governing transition intensities are different in the two cases because they are related to different molecular properties. Raman may be used to characterize certain classes of bonds as well as identify crystalline polymorphy of differ-

ent organic and inorganic materials. The Raman spectrometer system consists of four basic components:

Monochromator. Special holographic laser notch filters have radically changed the design and efficiency of Raman instruments. A high-throughput (for all wavelengths other than the wavelength of the laser excitation) holographic notch filter can reduce the stray light ("photon fog") of elastically scattered radiation such that it does not swamp the signal at the detector. Available reduced-size monochromators suitable for a LRS system when used with a holographic notch prefilter have adequate stray-light rejection and resolution, and are even small enough to fit onto a PC card (Control Development Corp.).

Light sources. An important achievement is the development of single-mode laser diodes that are compact and lightweight, are 3–40% efficient, and have suitable luminescence for Raman spectroscopy (3–500 mW). These diodes can operate from 630 nm to longer wavelength (~780–810 nm) and induce less fluorescence background than shorter-wavelength sources do.

Fiber coupling. The third advance essential for a portable Raman instrument is in fiber optics, providing flexibility in sample excitation and data acquisition as well as permitting remote Raman spectroscopy with fiber probes as long as 1 km (Schoen, 1995). It is clear that fiber-coupled Raman systems are of great interest in designing a prototype Raman instrument for a planetary lander spacecraft. Deployment can be by (1) a passive appendage of the lander body that impales into the surface; (2) an active appendage of the lander or a rover in the form of a robotic arm; (3) transporting or trailing out from the lander vehicle by a microrover; (4) trailing behind an arrowlike projectile ejected from a combined projector/quiver.

Detection system. CCDs feature quantum efficiencies of up to 90% at wavelengths near 700–800 nm (9 of 10 incident photons are recorded). With sufficient cooling, which can be passive in most planetary environments (Mars, comets, etc.), they can be considered to be practically noiseless. Their two-dimensional nature (>10,242 pixels) enables multiple spectra to be acquired simultaneously. Using a gated intensified CCD with a pulsed diode laser will reduce the effect of interfering non-Raman long-lived luminescence of certain samples. There is now a considerable body of experience in dealing with cosmic-ray artifacts in CCD images (e.g., Hubble Space Telescope).

7.5.13. Scanning Electron Microscopy

"Environmental" SEM (ESEM, an electron microscope that tolerates relatively high pressures in the vicinity of the sample) would be useful for examining rock textures and mineral structures. In principle, it could also be used to detect microfossils, e.g., on Mars; however, the prospects for successful robotic detection of such microfossils seem remote at this time. Scanning electron microscopy is described in more detail in Chapter 6.

7.5.14. Secondary-Ion Mass Spectrometry (SIMS)

SIMS sensu stricto. Secondary-ion mass spectrometry (SIMS) is a useful technique in organic mass analysis as a means of volatilizing and ionizing species that are solid and would not be easily analyzable by conventional organic MS techniques. To prevent destruction of the molecular structure that one wishes to analyze, SIMS must operate within the so-called "static SIMS limit," i.e., the sample must receive a primary ion dose not exceeding 10^{12} ions/cm² (Katz, 1992).

Detection and analysis of secondary ions can be made using magnetic, quadrupole, or time-of-flight (TOF) mass spectrometers. When the analysis requires rapid acquisition of mass spectra over an extended mass range (above 500 Daltons), or when high mass resolution is desired, the TOF detection scheme becomes the preferred, if not the only, choice.

One of the most common modes of organic characterization involves the determination of a material's surface chemistry. This is accomplished through the interpretation of the fragmentation pattern in the static SIMS mass spectrum. This "fingerprint" yields a great deal of information about a sample's superficial chemical nature, including the relative degree of unsaturation, the presence or absence of aromatic groups, etc. Due to the low primary dose and absence of sputtering, static SIMS is mainly a surface analytical technique, with a penetration depth of about 10 Å.

Laser-based SIMS. If one wishes to analyze deeper than the sample surface, while not compromising its molecular structure, one can use a laser ablation/desorption system to effect the volatilization/ionization. Since lasers can be easily pulsed, they are naturally suited as ionization sources for TOF-type instruments. The mass-spectrometric analysis of high-molecular-weight compounds requires that the molecules, normally present in the condensed phase, be converted into intact, isolated ionized molecules in the gas phase. Two configurations are commonly used, one that uses a single laser to produce both the volatilization and the ionization of the substances of interest, the other of which decouples the volatilization (laser 1) and the ionization (laser 2). The latter configuration is often referred to as postionization (PI). Specific laser wavelengths can be used to ensure selectivity in ionization, thus creating the capability to search for specific classes of organic compounds (Hahn *et al.*, 1987; Zare *et al.*, 1988). This can be a valuable approach in a survey mode, to reduce and rationalize the complexity of molecular information in a natural system.

Another approach that can be useful in the analysis of large molecular structures is called Matrix Assisted Laser Desorption Ionization (MALDI). The "matrix" is a solid (typically a low-molecular-weight organic acid with an aromatic group) within which the analyte is dispersed. This absorbs the laser energy and redistributes it to the analyte while undergoing volatilization. As the volatilization takes place, a proton-rich environment is created that promotes ionization of the analyte via proton attachment. The value of

this scheme is that the matrix shields the analyte from excessive laser energy absorption, which would lead to its destruction (Hillenkamp *et al.*, 1991).

MALDI has been applied with success in the analysis of biopolymers such as proteins, carbohydrates, DNA, etc., as well as manmade organic polymers. Masses up to 150–200 kDa are routinely detected. Most of the applications of MALDI entail the use of specific matrices tailored to the analytes that are being sought. However, water ice can also act as a matrix, as demonstrated by the success in volatilizing and ionizing frozen DNA and protein-water solutions (Nelson *et al.*, 1989).

The value of a MALDI-type analytical instrument in a cometary lander is its potential ability to detect high-molecular-weight organic species dispersed in ice at the surface or in the interior of a cometary nucleus. Its strengths include the simplicity of a TOF mass spectrometer, the low weight of a laser unit, and the flexibility in wavelength, energy, pulse width, etc., made possible by recent technology.

7.5.15. Particle Desorption Mass Spectrometry (PDMS)

This is another mass-spectrometric technique that could be useful in the analysis of organic materials. Its principle is to use the fragments from spontaneous fission of ²⁵²Cf (half-life ~5 yr) to penetrate, desorb, and ionize organic molecules/fragments (Macfarlane and Torgerson, 1976). The ions thus formed are then analyzed using a TOF detection scheme. The start signal for the TOF measurement is provided by the complementary fission fragment. Two features make this type of ionization attractive for exobiological applications in space: One is the simplicity of the ionization source itself, which does not require a power supply because it is based on spontaneous fission; the second is the range of a Cf fission fragment in low-Z material, which is on the order of 15 µm, hence the sampling depth for this type of technique is considerably deeper than in the case of static SIMS discussed above. Commercial PDMS instruments exist and are currently used in biochemical analysis. A ²⁵²Cf-based instrument for planetary science would require a thin Cf source to be located at the ionization end of a mass spectrometer, a system for placing the sample in the source, and the appropriate electronics. A calculation of the required source activity depends on several parameters, including number of secondary ions desired, distance between Cf source and sample, and sample lateral size. For realistic sample- and spectrometer-size parameters, the source activity is calculated to be in the range of 10–20 µCurie, which is quite safe to prepare and to handle. The PDMS technique can be realistically used for detection of ions up to perhaps 2000 Da. This mass range could be considered complementary to MALDI.

7.5.16. Thermal Analysis

Thermal analytical techniques, especially when coupled with evolved-gas analysis, are powerful methods for characterizing a variety of substances. In particular, differential

thermal analysis (DTA) and the related technique, differential scanning calorimetry (DSC), can provide significant mineralogical information about unknown soil samples with relatively simple measurements (Wendlandt, 1986). In contrast to X-ray fluorescence, which gives only elemental-composition information about a sample, thermal analytical techniques can be quite specific regarding the mineralogical composition of soil samples. X-ray diffraction can also provide specific mineralogical information about soil samples, but volatiles and noncrystalline material are transparent to that technique. Infrared spectroscopic techniques are also capable of providing mineralogical data of samples. However, they cannot penetrate beneath the immediate weathered surface of a sample, leaving the unweathered bulk of the sample unanalyzed (Schwartz *et al.*, 1995).

DTA is a powerful analytical technique that can be used to identify the mineralogy of a sample. Of particular importance to exobiology is its ability to distinguish among clays, silicates, feldspars, zeolites, glasses, and evaporites, as well as to determine if organics are present. This is accomplished through the endothermic and exothermic processes associated with chemical reactions, phase changes, and other solid-state transition reactions occurring within the 0°–1200°C temperature range used. In DTA, the temperature of an unknown sample is measured differentially with respect to the temperature of an inert reference material, while the two samples are heated at the same rate simultaneously. As the temperature of the oven rises, any endothermic or exothermic reactions cause a change in the sample temperature relative to the reference. The size of the resulting exotherm or endotherm is indicative of the relative amount of material reacting (Schwartz *et al.*, 1995).

DSC, like DTA, monitors the temperatures of a sample and inert reference. Unlike DTA, DSC maintains the reference temperature isothermal with respect to the sample temperature during the heating process. The amount of heat required to maintain these isothermal conditions is then recorded as a function of time (or temperature). DSC is thus more quantitative than DTA because it measures directly the differential heat evolved or consumed (i.e., enthalpy) (Wendlandt, 1986). DTA is, however, less complex to implement than DSC (e.g., the mass of the sample must be determined in DSC, and the thermal contact between the sample and the cell wall must be tight and uniform). In contrast, data from DTA are not degraded when the mass of the sample is not known, nor does it require such tight control over the sample and cell-wall thermal contact (Wendlandt, 1986). An additional advantage to using DTA for geochemistry is that it can obtain accurate mineralogical information above 700°C. For example, clays exhibit a high-temperature transition between 950° and 1100°C that is critical to their identification. DSC cannot yield the enthalpy at these high temperatures and therefore cannot be used to distinguish accurately among the clays (Wendlandt, 1986).

7.5.17. X-Ray Diffraction/X-Ray Fluorescence

Many of the comments made earlier on the APX method apply also to X-ray diffraction/fluorescence (XRD/XRF). In this case, however, the ability to define mineralogy offers a more detailed and precise insight into the nature and role of aqueous processes involved in the formation of soils and sedimentary rocks. To the extent that X-ray analyses of rocks are possible, they would facilitate the identification of the lithologies (carbonates, cherts, clay-rich sediments) that are most promising for preserving a chemical record of preexisting aqueous environments, including a possible record of any now-extinct biology or prebiotic chemical evolution that took place in those environments. XRD/XRF is discussed in more detail in Chapter 6.

7.6. A NOTE ON INSTRUMENT ARRAYS, HYBRIDIZATION, AND NEW CONCEPTS

No single instrument, wavelength range, separation procedure, etc., is ever adequate on its own for carrying out analytical tasks in complex environments. That is why instrument hybridization occurs (discussed below), and why the analyst also brings a variety or array of instruments to bear on the sample. The lab chemist will use infrared (IR), laser Raman (LRS), ultraviolet/visible (UV/VIS), and nuclear magnetic resonance (NMR) spectroscopies, high-pressure chromatography (HPLC) and gas chromatography/mass spectroscopy (GC/MS), X-ray diffraction (XRD), and photoelectron spectroscopy (PES), etc., before coming to a conclusion about the nature of a substance. Being able to make a variety of measurements with an array of instruments is mandatory for good science in general. The architecture of the array must be considered carefully, and thus the spacecraft should not just carry a collection of individual instruments each playing its own tune, but must be an orchestra.

The keystone instrument of the array will be the general-purpose imaging system expected for all landers and, of course, roving vehicles. Other instruments also expected to exist as a matter of course are thermometers and barometers. Can these general-purpose instruments be configured with accessories (i.e., magnification, radiation thermometry instead of contact measurements) so they will have a greater dynamic range? Being able to make a spectroscopic measurement on a sample at different measured temperatures during a diurnal cycle(s) would transform a simple observation into a true experiment, characterized by varied parameters, with promise of a richer yield.

Certain instruments can also serve more than one role in that besides being a stand-alone, interrogating samples directly, they can also serve as a sensor in a more complex analytical system. The gas chromatograph/mass spectrometer (GC/MS) is the classic example of the hybrid instrument and the concept is expected to become even more widely used.

An example of what is to be expected is extension of the utility of the GC/MS with volatiles by adding, in parallel to GC, capillary electrophoresis (CE) (Harrison *et al.*, 1993), for species such as amino acids, and laser desorption (LD) of molecules such as polycyclic aromatic hydrocarbons (Kovalenko *et al.*, 1992). High-power pulses from compact diode lasers now make this possible on a spacecraft. The laser Raman spectrometer is another such an example. It can sense both an unprocessed sample, possibly at some distance via an optical fiber (Shoen, 1995), and a sample emerging out of a processor such as a gas chromatograph, via another optical fiber and surface-enhancement substrate (Roth and Kiefer, 1994).

Among the new and emerging technologies of interest for exobiological exploration are what have been referred to as the "New Microscopes." Utility for examining mineral samples suspected of harboring microfossils is obvious, but is by no means the only exobiological role for such instruments. Included are the scanning tunneling microscope (STM) and the atomic force microscope (AFM), with the AFM being of particular interest because the sample does not have to be conductive. Such an instrument is also of conventional utility for examination of crystalline texture. The dynamic range is very great, going from low magnification (100 $\times$) to atomic level. The actual instrument is compact and has negligible power requirements. The fact that it is a "table-top" instrument in the lab suggests that it probably can be used on a lander vehicle, including rovers at rest, with little problem. Also, because of its size and the fact that it does not require a vacuum, there is a clear advantage over electron-beam microscopes. However, because the piezoelectric transducer elements and allied circuitry operate at several hundred volts, attention must be paid to a potential electrical discharge problem in low-pressure environments, as on Mars.

There are also new optical microscope technologies, including scanning techniques, that result in improved performance relative to conventional microscopes (Betzig and Trautman, 1992). Another emerging microscope technology is the Raman microscope made possible by tunable filters (Treado and Morris, 1994; Pallister *et al.*, 1994). This allows imaging of a sample in terms of concentration of a molecular substructure such as hydroxyl or sulfate.

7.7. A NOTE ON MOBILITY AND SAMPLE ACQUISITION

Implicit in the foregoing has been ready access to the appropriate samples on the surface of Mars or another solar system body. However, achieving such access will certainly pose a number of technical challenges, such as (1) the need to transport the sampling apparatus from the landed spacecraft to the location of the sample of interest; (2) the desirability of acquiring a sample free of contamination by neighboring material (e.g., in the case of Mars, free of any surficial weathering products); and (3) the general need to manipulate the sample within the spacecraft (e.g., to move it from one

point to another and to fashion it into a shape and/or form amenable to analysis). Because these are engineering issues outside the areas of expertise of this writing group, and because in most cases these are issues that are not unique to exobiology but are confronted by landed-science in general, we do not address them in detail. However, we wish to emphasize the importance of work in these areas. In particular, from the perspective of exobiology, we believe that further development work is essential on the following issues:

Mobility on the martian surface. Despite recent advances in rover technology, further improvements in range and capability are still needed. Actual range requirement cannot yet be specified as it depends upon factors such as spatial resolution of orbital data, size of landing ellipse, and imponderables such as the geographic distribution of "interesting" terrain and safe landing sites.

Sampling beneath the oxidant layer on Mars. The most likely location where an organic record might have survived on the martian surface is within a fine-grained sedimentary rock. Consequently, a requirement for the exobiological exploration of Mars is the capability of extracting an interior sample of such a rock, using a process such as coring or chipping.

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